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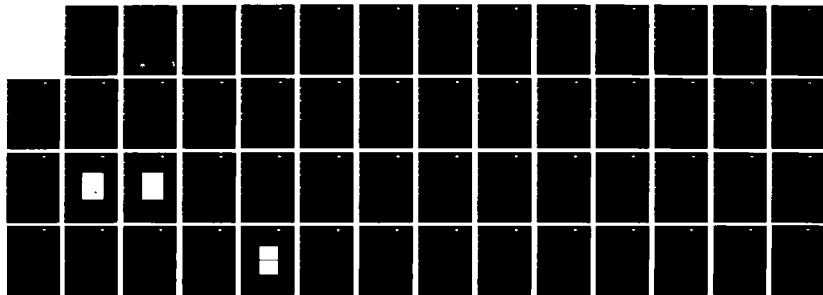
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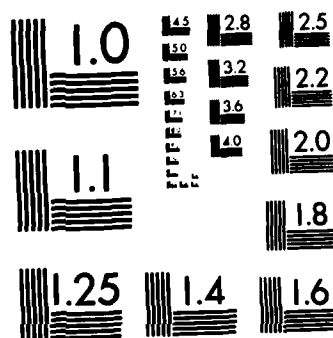
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**RESEARCH ON ELECTROLUMINESCENCE
IN THIN FILM YTTRIUM OXYSULFIDE**

**FINAL REPORT FOR THE PERIOD
June 1, 1981 through September 15, 1983**

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Prepared for

**Air Force Office of Scientific Research
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Washington, DC 20332**

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**Approved for public release;
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AUGUST 1984

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1.0 SUMMARY

The rare-earth oxysulfide phosphors have proven to be highly efficient phosphor materials for cathode ray tubes (CRT). Thin films of these phosphors have provided the highest brightness for a CRT reported to date.¹ The objective of this program was to evaluate the feasibility of fabricating thin film ac electroluminescent devices using the rare-earth activated oxysulfides. Rare-earth activators were chosen because their spectra covers the visible region and they are in general narrow line emitters. During this program electroluminescence was observed for the first time in thin film of rare earth host phosphors. Described in this report are the results of characterizing these thin film emitters. The characterization includes: 1) optical spectrum; 2) brightness-voltage curve; 3) photoluminescence; 4) x-ray diffraction; 5) annealing experiments. The characterization also includes comparative data on efficient rare earth cathodoluminescent powder phosphor material as well as high efficiency ZnS:Mn thin film EL emitter.

In summary, the results show that thin film ac electroluminescent devices can be fabricated using rare-earth activated yttrium oxysulfide material. The e-beam fabrication technique used is similar to that used to fabricate high efficiency ZnS:Mn thin film EL emitters at this laboratory. Presently the low observed EL intensity (fractions of a ft-L) is



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limited by the physical integrity of the film during elevated temperature annealing required for luminescence. Both photoluminescence and x-ray diffraction measurements indicate the optimum anneal temperature and time to be 900°C for one hour compared to the 600°C limit of the present 7059 glass substrate material. Through use of alternate substrate materials and/or an alternate annealing procedure, higher brightness electroluminescence should be achievable in these rare-earth thin film emitters.



2.0 BACKGROUND

The continued improvement in capability of military systems is due in large part to the use of increasingly complex solid state components. Many systems, however, are currently display limited for lack of a solid state replacement for the CRT, particularly where direct sunlight legibility, space, weight and power requirements are severe constraints.

Recent developments in flat panel matrix display technology offer solutions to many of the limitations of the cathode ray tube (CRT). In particular, thin film electroluminescence (TFEL) appears close to duplicating the operating characteristics of the CRT (shades of gray, high resolution, wide temperature range, true electronic mode of operation for long life color capability) while offering a dramatic decrease in weight, display volume and power requirements.

Using state-of-the-art TFEL materials a 20:1 reduction in weight and volume and a 10:1 reduction in power is possible over the conventional CRT terminal. Electro-optic brightness voltage measurements of state-of-the-art material indicate achievable brightness under matrix scan conditions of 200 ftL when operated at a duty cycle of 1/200 (200 line scan). For higher density displays (500-1000 lines) the duty cycle available for any one line drops proportionately so that the brightness is decreased to below 100 ftL. Legibility in direct sunlight, such as exists in a cockpit, requires at least a 200 ftL brightness. Therefore, an



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important extension of the TFEL technology could be achieved if the material exhibited a higher luminous conversion efficiency so that higher peak brightnesses were achievable under scan conditions. Current TFEL materials exhibit a luminous conversion efficiency of 5 lu/watt.²

CRT phosphors and fluorescent lamp phosphors yield 50-100 l/watt.³ A 10-fold improvement in a TFEL efficiency and instantaneous brightness could have a significant impact on high density matrix addressed display panels for cockpit use in direct sunlight.

Current TFEL phosphors utilize a zinc sulfide host matrix with various activators in order to produce the desired emission color. Previously, CRT phosphors also used the ZnS host. However, a significant increase in efficiency was made through the use of rare-earth activators. Certain members of the rare-earth oxysulfide phosphor family are among the highest intrinsic efficiency cathodoluminescent materials yet discovered.⁴

The rare earth host materials represent a more rigid crystal lattice as evidenced by the higher melting point of these materials compared with the zinc sulfide. This results in less phonon loss to the crystal lattice during the electron-to-light conversion process within the phosphor system. In addition, the higher temperature melting point characteristic insures a more stable phosphor when exposed to environmental extremes of heat and moisture. Rare earth activators typically exhibit a line spectra rather than a band spectra. This important



characteristic allows the emitted light to be confined to the photopic response spectrum of the human eye so that the luminous conversion efficiency is maximized. Also, the line spectra allows one to achieve better color purity in a multi-color display. Rare earth activators are available to provide the full color range (red, green, blue) required for a full-color display. These rare earth activators are more easily incorporated into the rare earth host crystal lattice compared with the zinc sulfide lattice.

Previous work by Buchanan¹ has demonstrated that thin films of the lanthum oxysulfide materials can be fabricated which exhibit good cathodoluminescence characteristics. These films were intended for use as the phosphor screen in a cathode ray tube. Additional requirements exist on the material properties in order to provide an electroluminescent display element. In order to elucidate those additional requirements on the thin film phosphor, a description follows of the light generating process and electro-optic characteristics of our current zinc sulfide manganese activated thin film EL devices.

2.1 EL Model

Figure 1 shows a cross-section of the display structure. A unique characteristic of this structure, using the ZnS:Mn, is the highly nonlinear electro-optic response of the emitter (Fig. 2). A model for this device has been proposed by this laboratory in which the nonlinear response is due to the nature of electron



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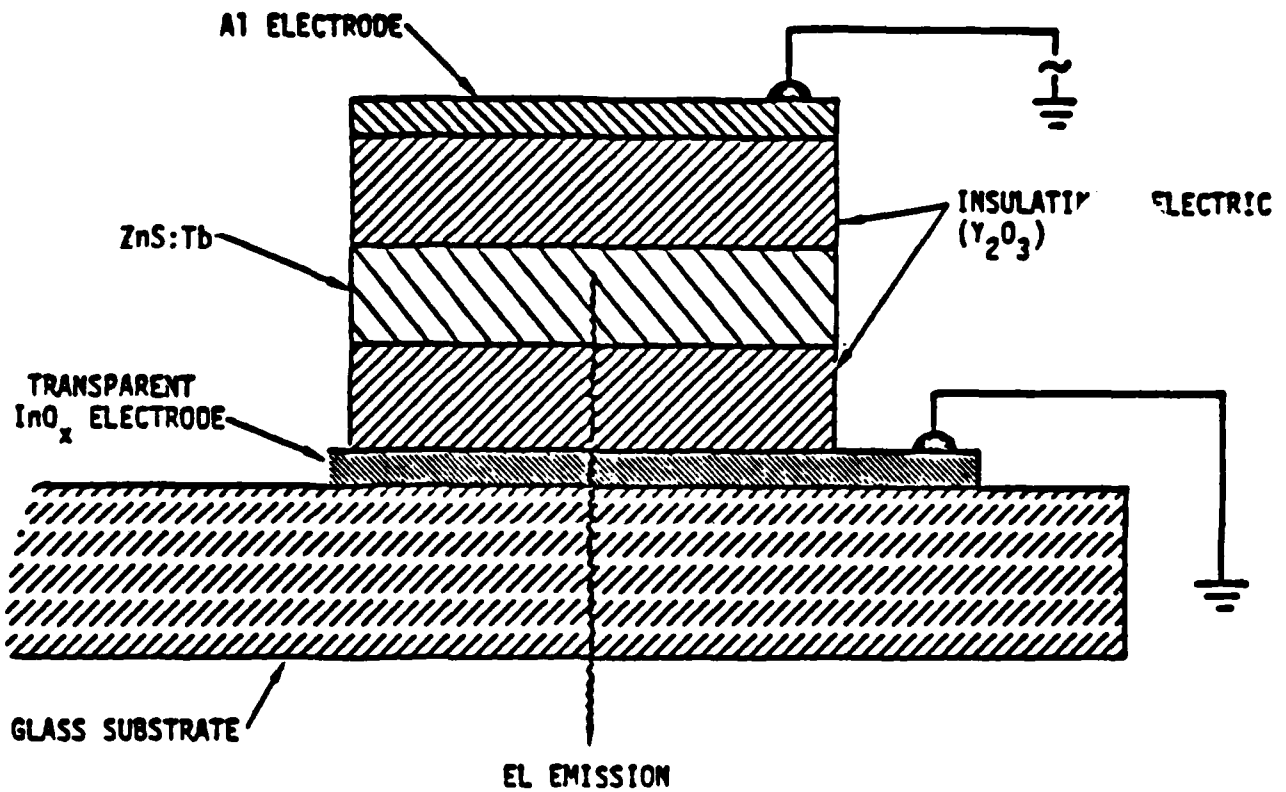


Fig. 1 Cross-section electroluminescent device structure.



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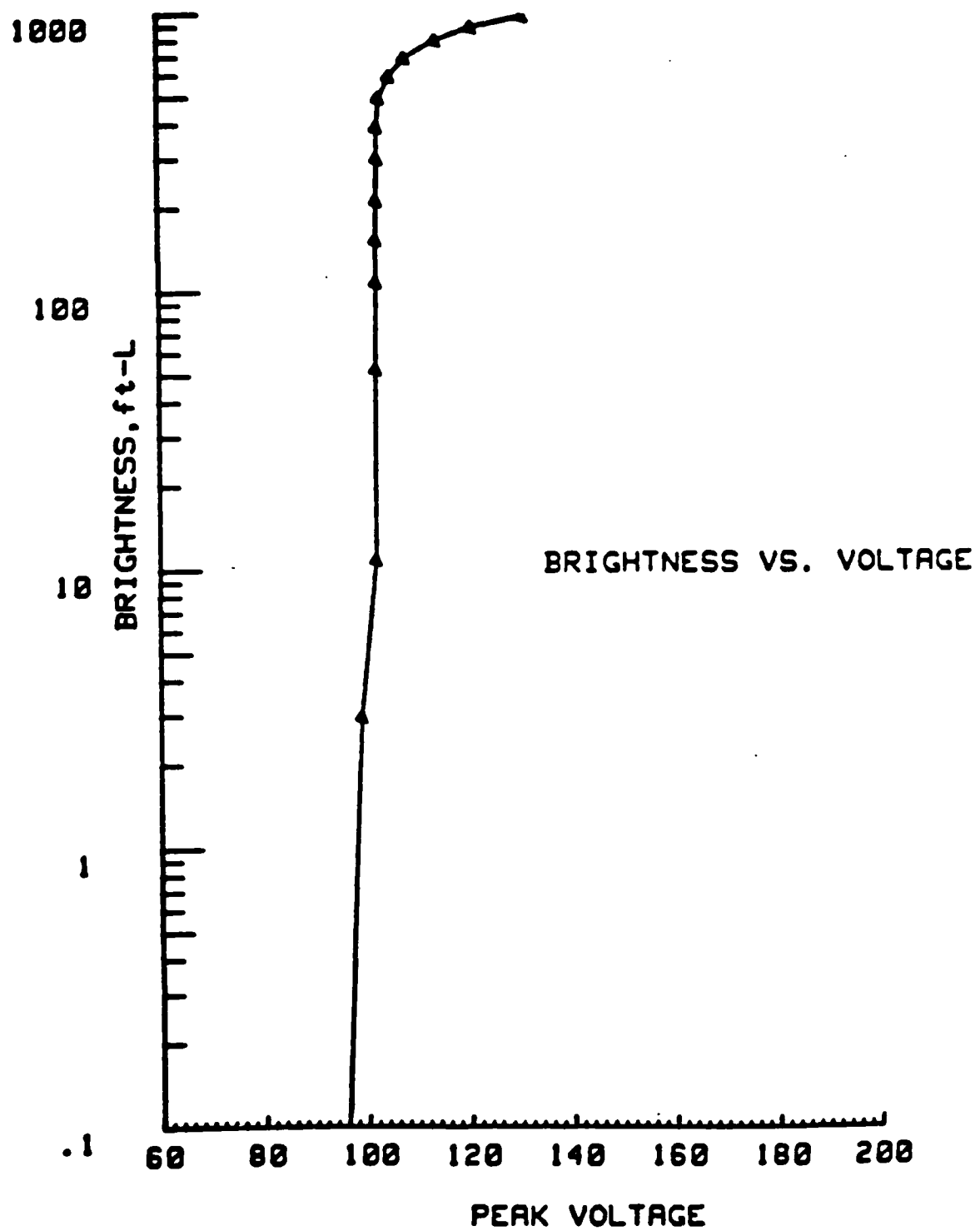


Fig. 2 Brightness-voltage for ZnS:Mn thin film emitter showing nonlinear response.



injection into the ZnS phosphor by a tunnel emission phenomenon.⁵ The tunnel emission characteristic is relatively independent of temperature, which implies that a display of this type can be operated over a wide temperature range.

The model attempts to explain the mechanism of initiation of electroluminescence in ZnS:Mn films. The basic assumptions are:

1. Electrons from unidentified donor levels become trapped at the ZnS:oxide interface.
2. The trapped electrons are very long lived and are only released at high ($\sim 10^6$ v/cm) field strength by tunneling.
3. These electrons, when released at high fields, quickly become very energetic and impact excite the active Mn center in the ZnS layer, causing luminescence.
4. The electrons then become trapped again to be re-released on the opposite polarity swing of the voltage cycle.

Figure 3 illustrates schematically the one-dimensional model for the interface states in the presence of a large electric field. This simple one-dimensional model assumes that electrons vibrate in a one-dimensional well with frequency $\nu(E)$ and that they can tunnel with a probability of tunneling given approximately by the WKB approximation:

$$T(E,F) \exp - \frac{AE^{3/2}}{F}$$



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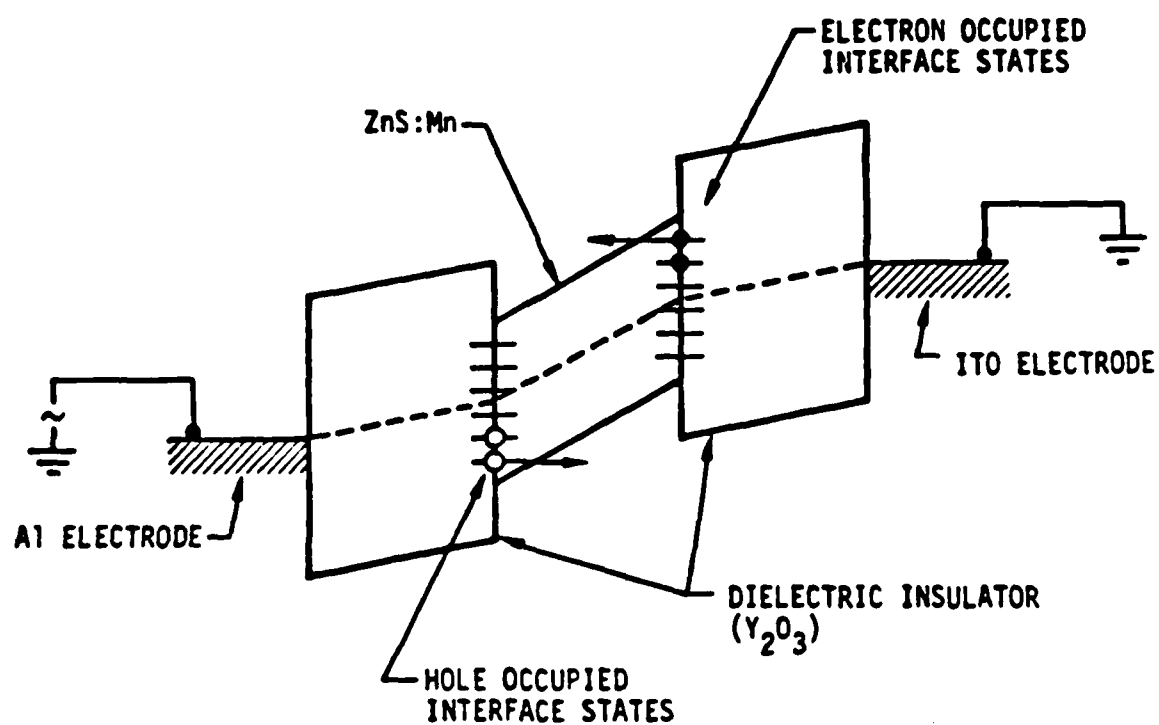


Fig. 3 One-dimensional model of interface states in presence of large electric field.



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where E is the energy level of the interface trap and is measured from the top of the conduction band, and F is the field across the ZnS. It is assumed that all the surface state density is concentrated in a level E_1 . The current density is given by

$$j(t) = n_1 \nu(E_1) T(E_1, t)$$

where n_1 is the number of electrons at E_1 , $\nu(E_1)$ is the vibrational frequency of the electron, and $T(E_1, t)$ is the tunneling probability. The current rises steeply with field so that most of the charge is transported at $j=j_{\max}$ corresponding to $F = F_{\max}$. A plot of $\ln j_{\max}$ versus $1/F_{\max}$ should give a value for E_1 the interface level.

Figure 4 is a plot of $\ln j_{\max}$ vs. $1/F_{\max}$ for an EL device made at this laboratory. The interface level of 0.4ev was obtained from the slope of the curve. In addition, the invariance of the tunneling current as a function of temperature is also shown.

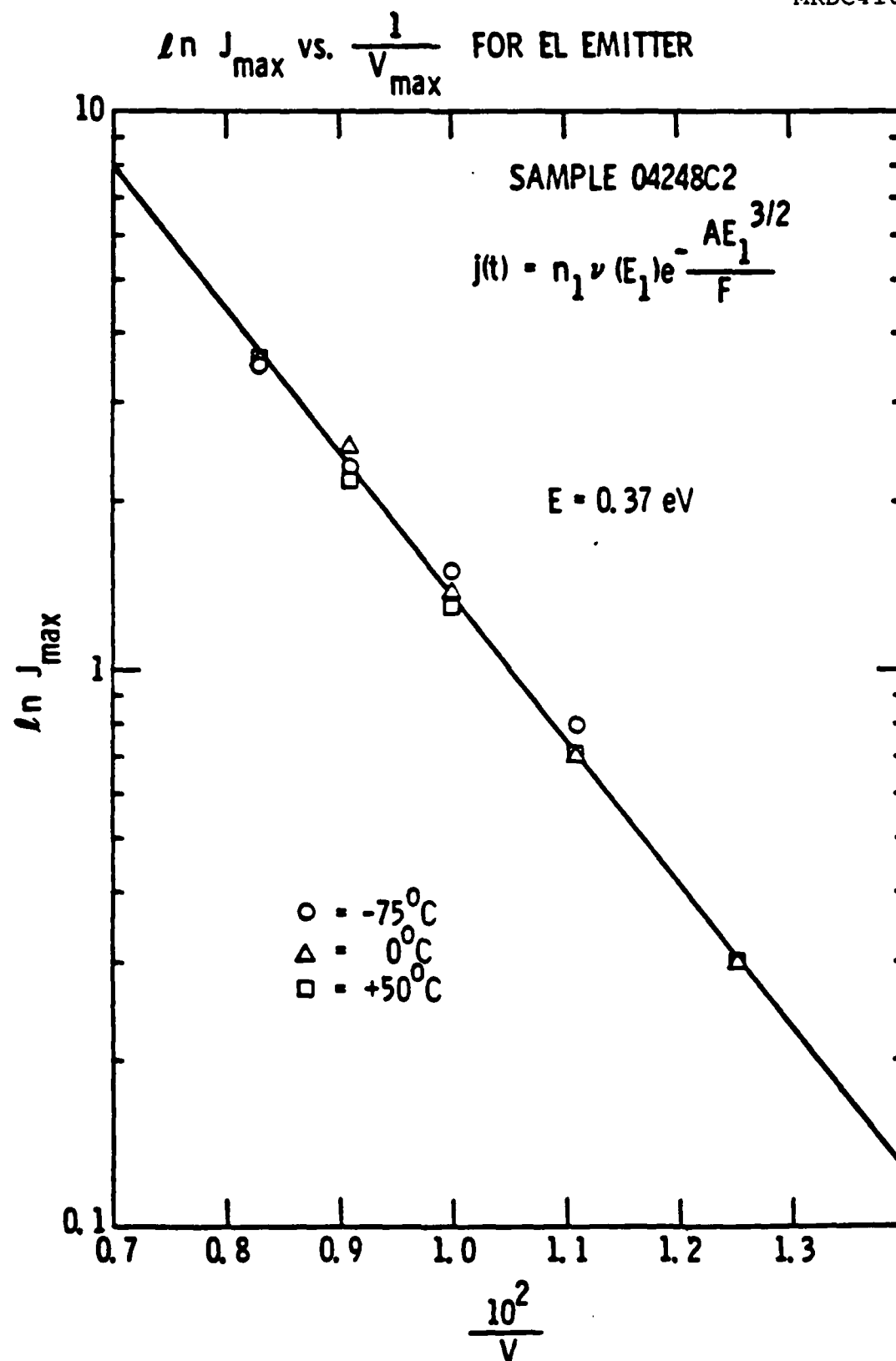
It should be stressed that we are discussing tunneling field emission, not the Frenkel-Poole effect. The latter is the field induced lowering of the thermal emission barrier. In the Frenkel-Poole effect the log of current density is proportional to $\nu^{1/2}$. However, the Frenkel-Poole effect is strongly temperature dependent while the tunneling emission is not.

2.2 Requirements for Thin Film EL Materials

The luminescent property requirements are similar to those for cathodoluminescence films. That is, efficient absorbtion of



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Fig. 4 Plot of $\ln J_{\max}$ vs $1/F$ for thin film emitter.



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hot electrons by the activator sites, efficient radiation of this energy in the optical wavelength visible to the human eye. However, in the case of the electroluminescent film, electron injection and transport to the activator site must be provided by the electrode structure on the film rather than from external high velocity electrons injected from an electron beam source. The requirements for a transparent host crystal are similar so that the light generated reach the observer's eye with minimum attenuation. The film should be stable with exposure to heat and moisture conditions so that the display panel can be fabricated by normal photolithographic techniques. The film should have a minimum of impurity ions that would tend to drift under electric field application. The material should be capable of being fabricated in a continuous form so that high electric fields can be applied to the device without breakdown through the film. The material must be compatible with conductive electrodes so that the electric field can be applied to the phosphor film. An electron injecting contact is required, particularly of the tunnel emitter type so that the threshold type response can be preserved for matrix panel addressing. The film must be capable of electron transport of hot electrons so that the injected electrons can reach the activator site. The activator itself must be stable under high electric field so that no drift within the crystal lattice occurs that would distort the electric field or destroy the electroluminescence of the film.



3.0 MATERIALS FABRICATION

Films of $Y_2O_2S:Eu$ were produced by reactively E-beam depositing Y_2O_3 in an H_2S atmosphere as well as direct E-beam deposition of Y_2O_2S phosphor. In the case of the Y_2O_3 activated deposition, the europium activator was provided by co-deposition of EuF_3 . Variables investigated included background gas concentration, substrate temperature, activator concentration, post-annealing conditions, substrate material, host material thickness, and use of overlay-capping anneal.

The general structure utilized for test employed a dielectric of Y_2O_3 on either side of the rare earth host phosphor (see Fig. 1). For the typical zinc sulfide EL emitter this sort of a structure allows near breakdown fields to prevail within the host so that in-phase electronic current can be provided for impact excitation of the activator. The adjacent dielectrics on either side of the phosphor limit the current available at the breakdown field conditions so that thermal runaway and destruction of the device does not occur. Typically the devices fabricated under this program employed an initial dielectric layer of yttrium oxide (1500 angstroms) deposited on the transparent conductive ITO (indium tin oxide) coated substrate. ITO conductivity was 15 ohms/square. The ITO was configured on the substrate such that individual segments 2 mm wide by 4 mm long could be electrically addressed. Each substrate was one inch by three inches in area and contained 30 such segments on a



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substrate for test. After E-beam deposition of the first Y_2O_3 , the Y_2O_2S was E-beam deposited in the same vacuum pump-down. The rate of deposition was controlled by a quartz crystal monitor at approximately 3 angstroms per second. Substrate and sidewall temperatures were monitored and controlled through use of thermocouple sensors. Background gas pressure was monitored with an ion gauge sensor and manual control used to maintain the pressure background. Following the phosphor host deposition, the substrate was removed from the vacuum chamber and heat treated in a separate high temperature tube furnace capable of $900^{\circ}C$ operation. This tube furnace had the facility for background gas control under several hundred microns gas pressure. In some cases, a third layer was E-beam deposited prior to removal from the vacuum chamber in order to act as a cap during the high temperature anneal. Following the anneal step, the second dielectric (typically Y_2O_3) was E-beam deposited. Finally aluminum electrodes were vacuum deposited through a mask.

Films deposited by the reactive deposition of Y_2O_3 and H_2S with a co-deposition of EuF_3 as the activator did demonstrate low intensity red electroluminescence typical of the europium +3 ion. Intensity of the electroluminescence was apparently limited by the mechanical integrity of the host phosphor material. That is, as a result of high temperature annealing, the Y_2O_2S material tended to craze from the substrate. Therefore, a major part of the effort was devoted to determining techniques for forming the host phosphor on the substrate while maintaining continuous film



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characteristics so that high electric fields could be applied to the device. The variables included in this investigation were substrate temperature during deposition, substrate material, anneal temperature, anneal background gas, rise and fall time of anneal cycle, over-cap drying anneal step, post deposition material.

3.1 Substrate Temperature

In general, the higher the substrate temperature during deposition, the more stable the deposited film is with respect to physical properties. Substrate temperature was varied between 200°C and 260°C with minimum effect on the crazing problem of the deposited film upon anneal. A deposition run of 320°C was aborted due to failure of the water-cooled quartz sensor that was used to monitor the deposition rate.

3.2 Substrate Material and Preparation

Sapphire was evaluated as a substrate material with a closer coefficient of thermal expansion to the Y_2O_3 deposited film. The coefficient of expansion for the normally used 7059 Corning Glass substrate material is $4.6 \times 10^{-6}/^{\circ}C$. Compared with $8.0 \times 10^{-6}/^{\circ}C$ for the sapphire material, little effect was seen on the crazing problem through the use of the alternate substrate material. However, the sapphire melting point is 2000°C so that optimum annealing temperature at 900°C could be readily accommodated on this material. The upper limit for the 7059 is



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approximately 700°C. Also, in each deposition an alumina ceramic substrate was included to allow evaluation of cathodoluminescence under high temperature anneal conditions.

Typically each substrate was prepared using a detergent wash with a mechanical brush scrubbing followed by DI water rinse and finally dried using a two-step acetone, methanol dip with a nitrogen blow-off. Prior to deposition a 10-minute glow discharge was performed in the chamber as further substrate preparation. In the case of the sapphire substrate material, since a grinding operation has been performed, a special cleaning procedure was used as recommended by the sapphire manufacturer. The cleaning consisted of soaking in a 30:70 mix by volume of $\text{H}_2\text{O}_2:\text{H}_2\text{SO}_4$ for 30 seconds. The part was then rinsed in DI water followed by methanol rinse and then blown dry with a nitrogen gun. In the same deposition a sapphire substrate was cleaned by the standard procedure (non-acid soak). There was no observable difference in the degree of cracking after anneal comparing the two sapphire substrates.

3.3 Background Gas During Deposition Process

The background gas pressure was varied from 5×10^{-5} Torr to 2×10^{-4} Torr of hydrogen sulfide. The purpose of the hydrogen sulfide is to reactively convert the Y_2O_3 to $\text{Y}_2\text{O}_2\text{S}$ during a deposition. For the case of the reactively formed $\text{Y}_2\text{O}_2\text{S}$, one would expect a narrower bandgap and hence higher leakage currents as the sulphur content was increased compared with plain Y_2O_3 ,



based on the differences in bandgap. Later experiments using the activated phosphor material (which already contained sulphur in the powder source) indicated that the sulphur content in the deposited film was very close to that in the starting pellet. Therefore, on succeeding depositions with the activated phosphor material, no additional H_2S was added to the background gas during deposition.

In the case where the H_2S pressure was varied by a factor of 5:1 between two separate depositions of Y_2O_3 , a maximum change of 3% increase in the sulphur content resulted in the as deposited film. A more significant change resulted during anneal in which typically 12-15% of the sulphur was lost. Through use of the activated phosphor powder as the starting source material a yttrium to sulphur concentration ratio in the annealed film very comparable to that of the starting material could be obtained.

3.4 Rise and Fall Time of the Anneal Cycle

Previous experience with zinc sulfide thin film emitters with an underlying dielectric of Y_2O_3 showed that the composite film structure was little affected during the $600^\circ C$ anneal by rapid temperature increases ($60^\circ/\text{minute}$) as well as with moderately short cool-down times ($20^\circ/\text{minute}$). In the case of the Y_2O_2S host which typically exhibited crazing upon annealing, rise and fall times were varied between 60 and $6^\circ/\text{minute}$ rise time and between 20 and $2^\circ/\text{minute}$ fall time after anneal. The longer cool-down times did result in less gross crazing, however



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microscopic cracks were still visible under the microscope in all cases. The one exception was the activated phosphor powder deposition upon a sapphire substrate which contained no ITO. The more violent cracking in general was associated with the ITO coated areas indicating a chemical reaction occurring between the two compounds. That is, the cracking resulted in de-lamination of the ITO from the underlying glass substrate. Layers deposited using the activated powder source yielded deposited films closest to the stoichiometric ratio of yttria to sulphur as determined from the powder material itself and also exhibited the least cracking. Most likely the severe cracking is due to the non-stoichiometric ratios produced by the reactive deposition at the glass substrate.

3.5 Thin Film Overcap During Anneal

In the fabrication of the normal zinc sulfide manganese activated TFEL emitters it has been found that annealing of the Y_2O_3 film by itself at $600^\circ C$ will result in cracking of the dielectric. However, if that same film is overcoated with a half micron of zinc sulfide the combination layer will remain intact through the anneal. Therefore, several depositions were made in which a third thin film layer of zinc sulfide was deposited over the first two layers (Y_2O_3 , Y_2O_2S) prior to the anneal of the completed structure. The results of this experiment do indicate that much less cracking occurs in the over-coated area under the zinc sulfide. However, micro cracks are still visible under



microscope examination. One such film as described was operated above 100 volts peak and did show blue emission typical of the self-activated zinc sulfide EL material. This would indicate that an electric field of at least 2×10^6 volt/centimeter was obtained in the zinc sulfide. No electroluminescence from the europium site was detected, however. Based on the relative ratios of the dielectric constant for yttria oxysulfide, yttrium oxide and zinc sulfide it is estimated that a comparable field (2×10^6 volts/centimeter) existed in the yttria oxysulfide during this measurement. Electronic in-phase current was observed in this test sample. However, this current was most likely due only to the zinc sulfide material.



4.0 PHYSICAL PROPERTIES

4.1 X-Ray

In evaluating the rare-earth oxysulfide thin films, measurements were made on their physical properties and compared to the CRT powder phosphor material. X-ray diffraction measurements were made in order to determine whether the Y_2O_3 had been converted to Y_2O_2S . In addition SEM-EDAX measurements were made to determine the ratios of yttrium to sulfur and yttrium to europium as a function of the depositions and anneal process. These SEM results were compared to the standard CRT powder phosphor material.

The films, which were produced by electron-beam evaporation from a Y_2O_3 pellet in a sulfur background were subjected to several different anneal time-temperature profiles. Some films were annealed in an argon atmosphere at $600^{\circ}C$ for one hour. After anneal these films turned black and the film appeared crazed. The crazing appears to be caused by the mismatch in thermal expansion between the glass and oxysulfide films.

All other films were annealed in an atmosphere of 10% SO_2 and 90% H_2 . The films appeared pale yellow before anneal and were colorless after anneal. During each deposition both 7059 glass and ceramic (Al_2O_3) were used as substrates. Those films deposited on the 7059 glass were annealed at $600^{\circ}C$ for 1 hour. In order to make them into electroluminescent devices, a second dielectric layer was deposited and finally the rear Al electrode.



The films on the Al_2O_3 substrate had both the first dielectric (Y_2O_3) and the oxysulfide film. These films were subjected to a series of time-temperature profiles in the hydrogen plus sulfur dioxide atmosphere. Some were annealed at 900°C for 1/2, 1, 3 hours. Others were annealed at 600°C for 1/2, 1, 3, 5 hours.

The x-ray diffraction patterns of these films indicate that the optimum time and temperature is 900°C for 1 hour. The films annealed at 600°C for 5 hours had a diffraction pattern that was similar to the unannealed film, which showed very little structure. From this data it is difficult to determine whether the films are predominantly Y_2O_3 or $\text{Y}_2\text{O}_2\text{S}$. This will be discussed further in the section on photoluminescence.

Some films were evaporated from a source material that was fabricated from a CRT phosphor powder with europium as an activator. This source material also had about 12 atomic percent copper. The films made from this material were annealed at 600°C in a nitrogen atmosphere. These devices experienced the same crazing as those films made by reactive evaporation. However, films made from the phosphor powder that were evaporated onto sapphire substrates without ITO or yttria did not experience crazing after being annealed at 600°C for one hour.

X-ray diffraction patterns of the films prepared from the phosphor powder which were annealed at 600°C for one hour indicate they are more crystalline than comparable films prepared by reactive evaporation. However, when these films were



deposited directly onto ITO, there appears to be a reaction between the oxysulfide and the ITO creating a different compound at the interface. This phenomenon is not observed on samples with the yttria between the ITO and oxysulfide. There was a significant improvement in the crystallinity of these films after annealing at 600°C for one hour in nitrogen. Further improvement could be expected at 900°C. In addition the unannealed samples showed a weak oxysulfide pattern which had not been observed with the reactive evaporated films. These results indicate it is possible to obtain oxysulfide films without the added complexity of annealing in an H₂S or SO₂ atmosphere.

4.2 SEM-EDAX

Films deposited on 7059 glass and ceramic (Al₂O₃) substrates were examined both before and after anneal at 900°C, using the scanning electron microscope (SEM). Figure 5 is an SEM photograph at 1×10^4 magnification of the annealed film. The large particles are the Al₂O₃ substrate. Because the ceramic substrates consisted of these large particles it was difficult to determine if the films crazed at 900°C. SEM photographs of the film annealed on 7059 glass are shown in Figure 6. The area analyzed was the phosphor area with the ITO and first dielectric layer underneath. The crazing of the film is probably due to the mismatch in thermal expansion of the glass and the Y₂O₂S film.

In addition to the SEM, the EDAX (energy dispersive analysis by x-ray) was used to determine the composition of the various



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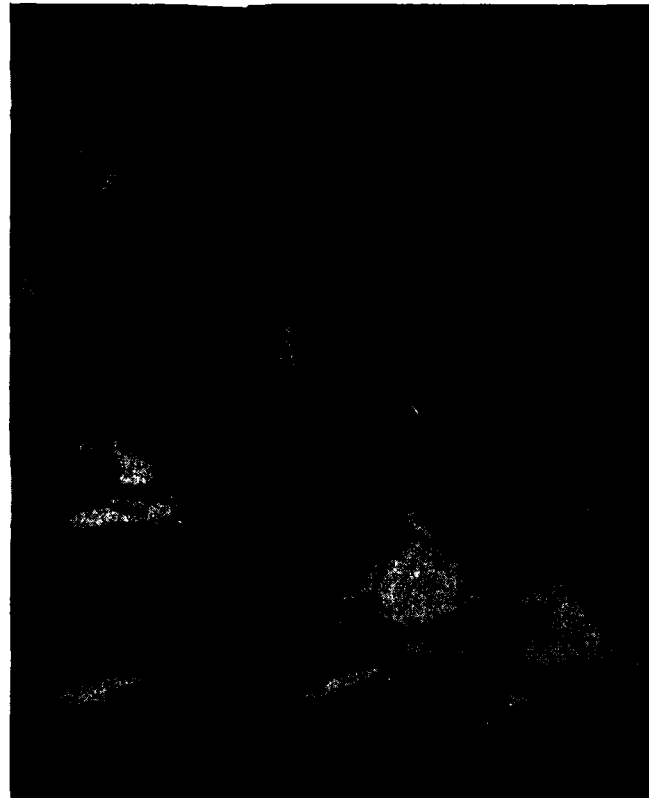


Fig. 5 SEM photograph of annealed oxysulfide film on Al_2O_3 showing cracks. Annealed for 1 hour at 900°C .



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Fig. 6 SEM photograph of annealed oxysulfide on 7059 glass showing crazing. Annealed for 1 hour at 600°C.



evaporated films. The phosphor powder was used as a reference. The results of this investigation indicate that annealing causes a loss of sulfur and has no effect on the europium concentration. Films prepared reactively were sulfur deficient. These films required annealing in a sulfur atmosphere to make them more stoichiometric. The films prepared from the phosphor powder were sulfur rich as deposited. These films were annealed in a argon atmosphere. During the anneal procedure the films lost sulfur, such that, the final composition was closed to the starting material.



5.0 ELECTRO-OPTICS

5.1 Photoluminescence Measurements

Several electro-optic measurements were performed on the $(Y_{1-x}, Eu_x)_2O_2S$ thin films. These consisted of: 1) emission spectra; 2) photoluminescence spectra; 3) brightness-voltage curves. The emission spectra were obtained using a Jarrel-Ash 0.5m monochromator and a PAR lock-in amplifier.

Photoluminescence measurements were performed on the $Y_{1-x}, Eu_x)_2O_2S$ thin films as a means of determining the transitions of the europium activator. In addition, photoluminescence was used to determine the optimum heat treatment. Previous work with ZnS:Mn thin films indicated that in general photoluminescence increased significantly after the anneal procedure as did the electroluminescence. For the oxysulfide films produced on Al_2O_3 it was not possible to perform electroluminescent measurements since no electrodes were included.

The crystal field establishes in part the oscillator strengths of the $4f^6$ transitions of the rare-earth ions. For the free Eu^{+3} ion, all the $4f^6$ transitions have the same parity; therefore, only magnetic dipole and quadrapole transitions can occur. In this case the electric dipole transitions are forbidden. When the symmetry of the crystal field lacks a center of inversion electric dipoles are allowed. The emission spectra observed with $(Y_{1-x}Eu_x)_2O_2S$ films show both magnetic and electric



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dipole transitions indicating that the Eu^{+3} ion is located at a site lacking inversion symmetry.

In rare-earths, transitions among the f-electron energy levels results in line emission because the outer shielding electrons minimize the perturbing influence of the crystal field. Whereas, in the more usual case involving d-electrons, considerable perturbation occurs, resulting in broad emission bands.

Photoluminescence of $\text{Y}_2\text{O}_2\text{S:Eu}$ shows the sharp line europium emission. Figure 7 shows the emission spectrum of a $\text{Y}_2\text{O}_2\text{S:Eu}$ CRT powder phosphor which was used as a reference.⁶ The dominant lines are at 6270 ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) and 7070 ($^5\text{D}_0 \rightarrow ^7\text{F}_4$) both electric dipole transitions. There are several weaker lines most of which are magnetic dipole transitions. The ones of interest which also appear in the thin films are at 5960 ($^5\text{D}_0 \rightarrow ^7\text{F}_1$) and 5400 ($^5\text{D}_1 \rightarrow ^7\text{F}_1$).

Figures 8a,b,c show the effect of annealing the thin films at 900°C for various times. The unannealed film (Fig. 8d) has major line at 6160 ($^5\text{D}_0 \rightarrow ^7\text{F}_2$), 5600 ($^5\text{D}_1 \rightarrow ^7\text{F}_2$) and a broad unresolved peak at about 5000 angstroms. The shift in the major peak at 6160 could be due to the influence of the crystal field of the amorphous films or it could be that the films are sulfur deficient and appear like Y_2O_3 . The x-ray diffraction patterns are too weak to be able to differentiate. The EDAX data seems to indicate that the sulfur to yttrium ratio is close to that of the CRT powder. This would seem to indicate that the films are $\text{Y}_2\text{O}_2\text{S}$



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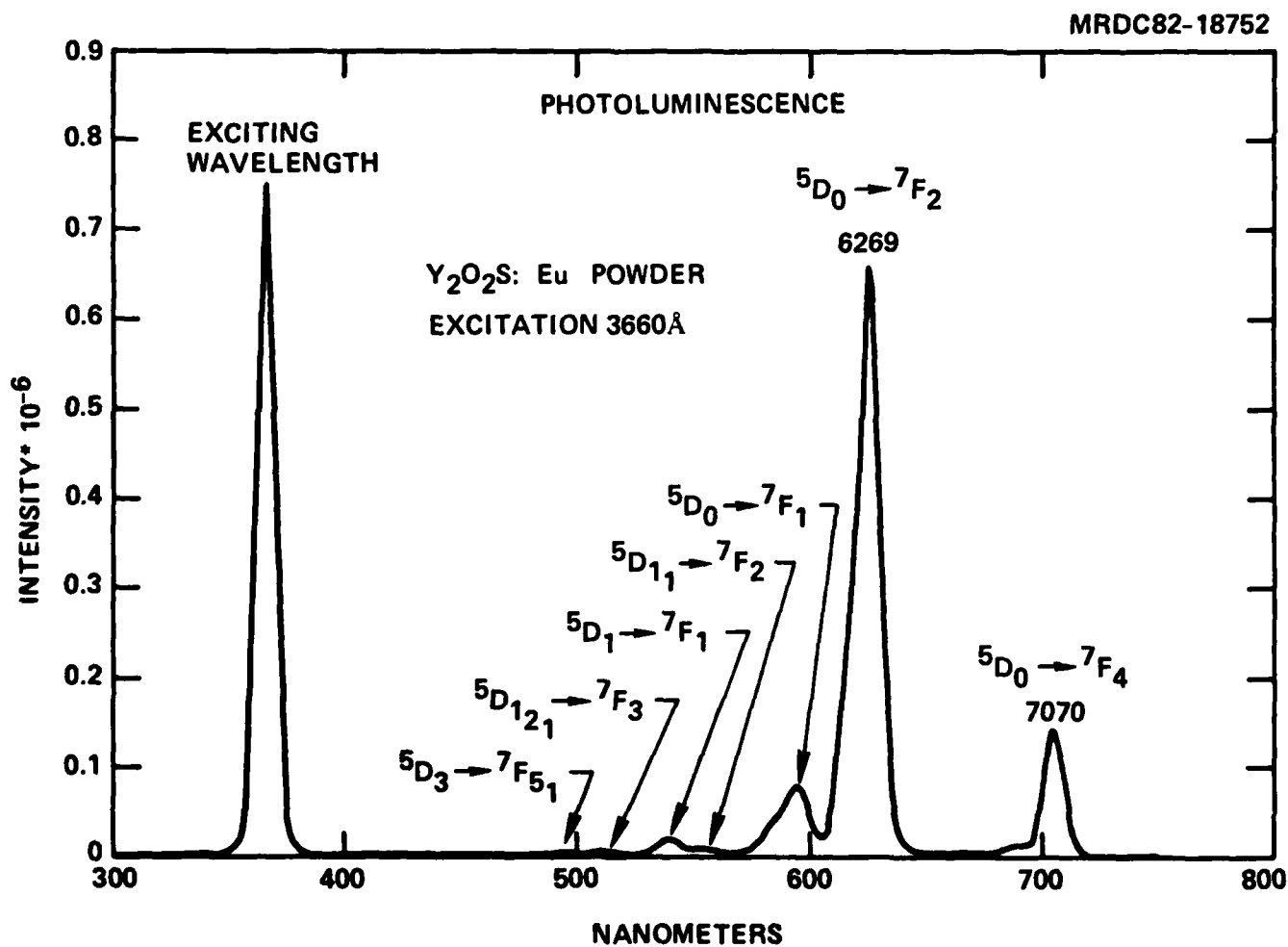


Fig. 7 Photoluminescent spectrum of yttrium oxysulfide europium powder used as CRT phosphor.



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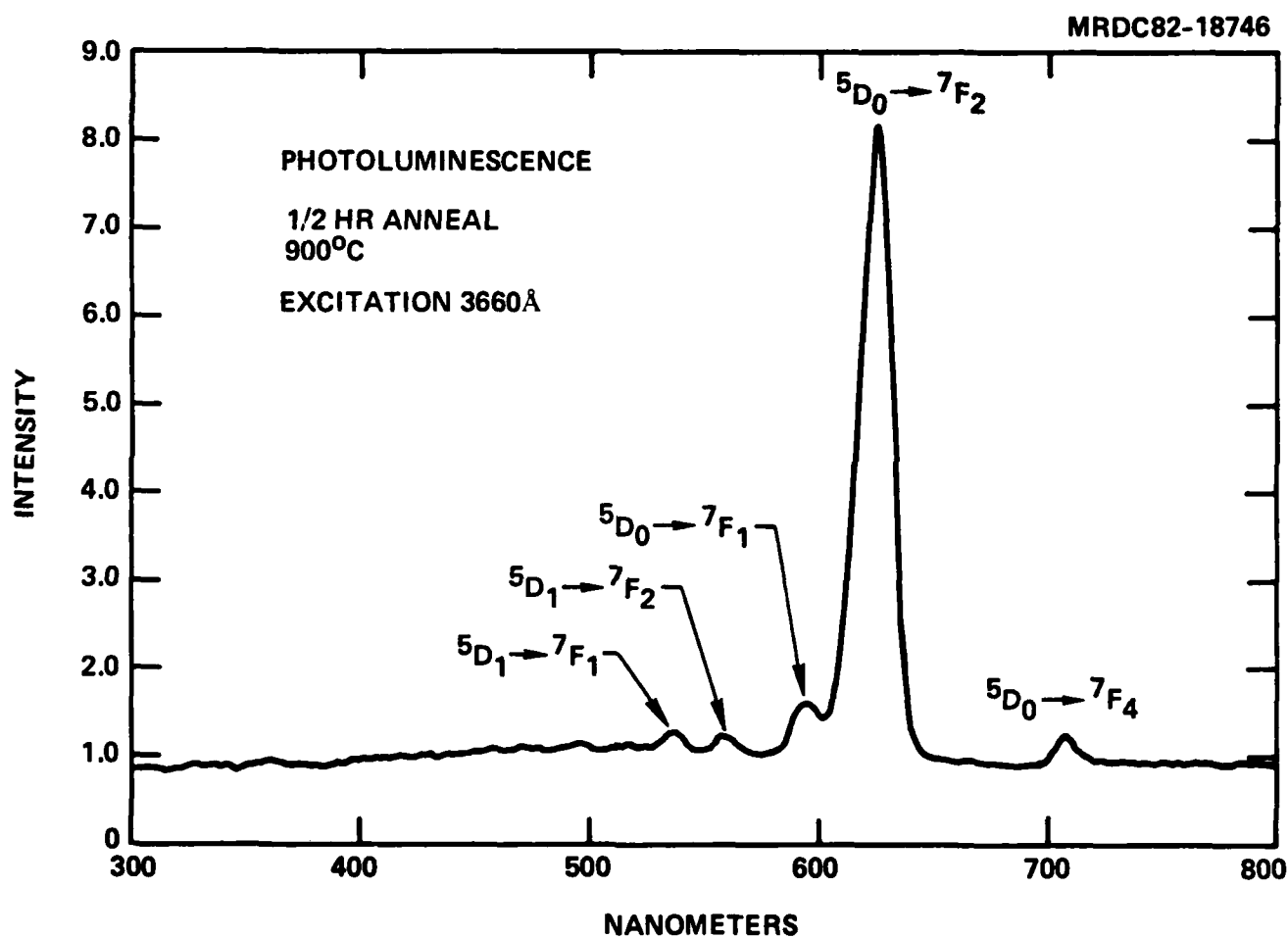


Fig. 8 Photoluminescent spectrum of $\text{Y}_2\text{O}_3\text{S: Eu}^{+3}$ film on Al_2O_3 .
(a) Annealed for 1/2 hour at 900°C.

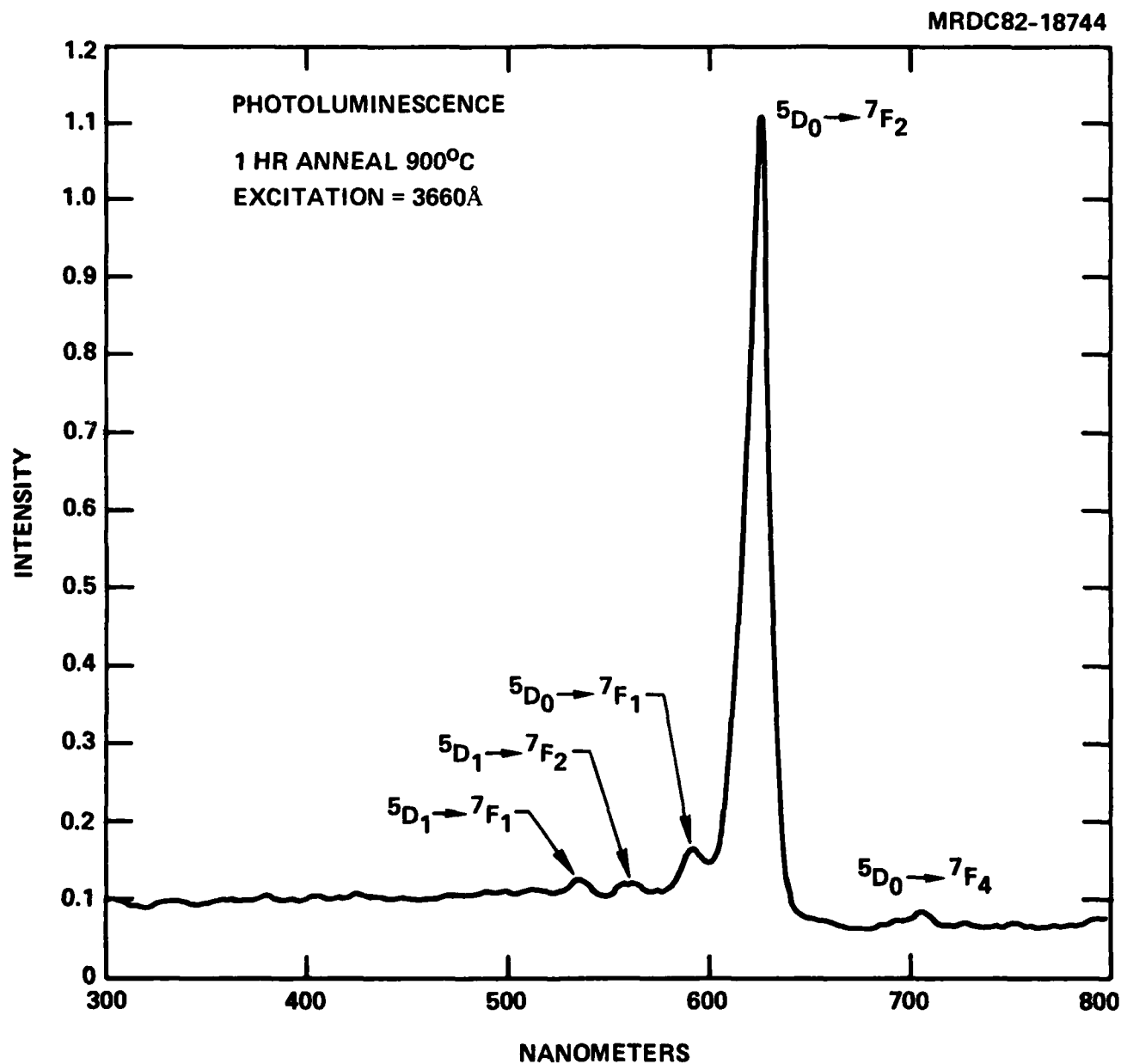


Fig. 8 (Cont.) (b) Annealed for 1 hour at 900°C.



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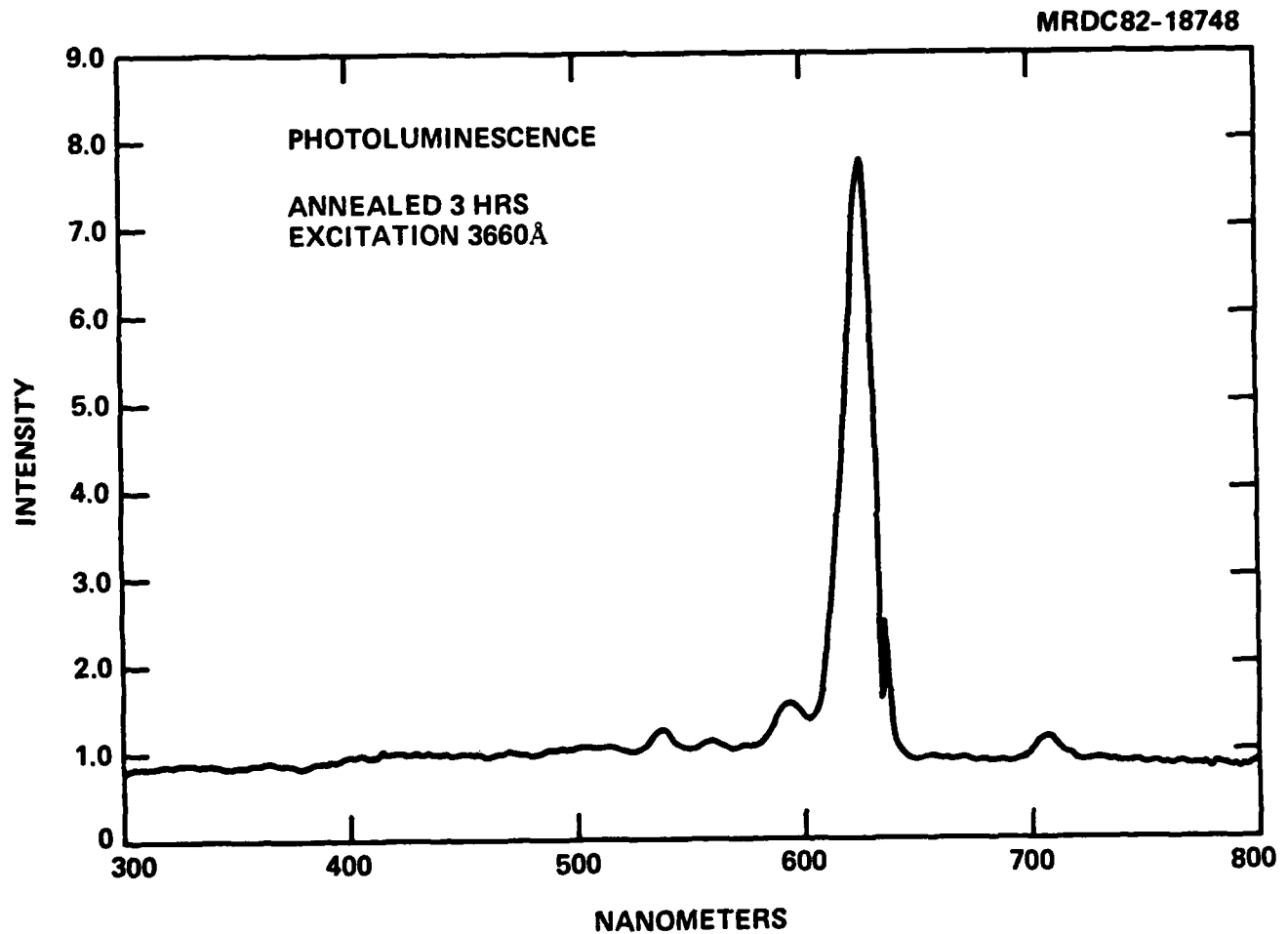


Fig. 8 (Cont.) (c) Annealed for 3 hours at 900°C.



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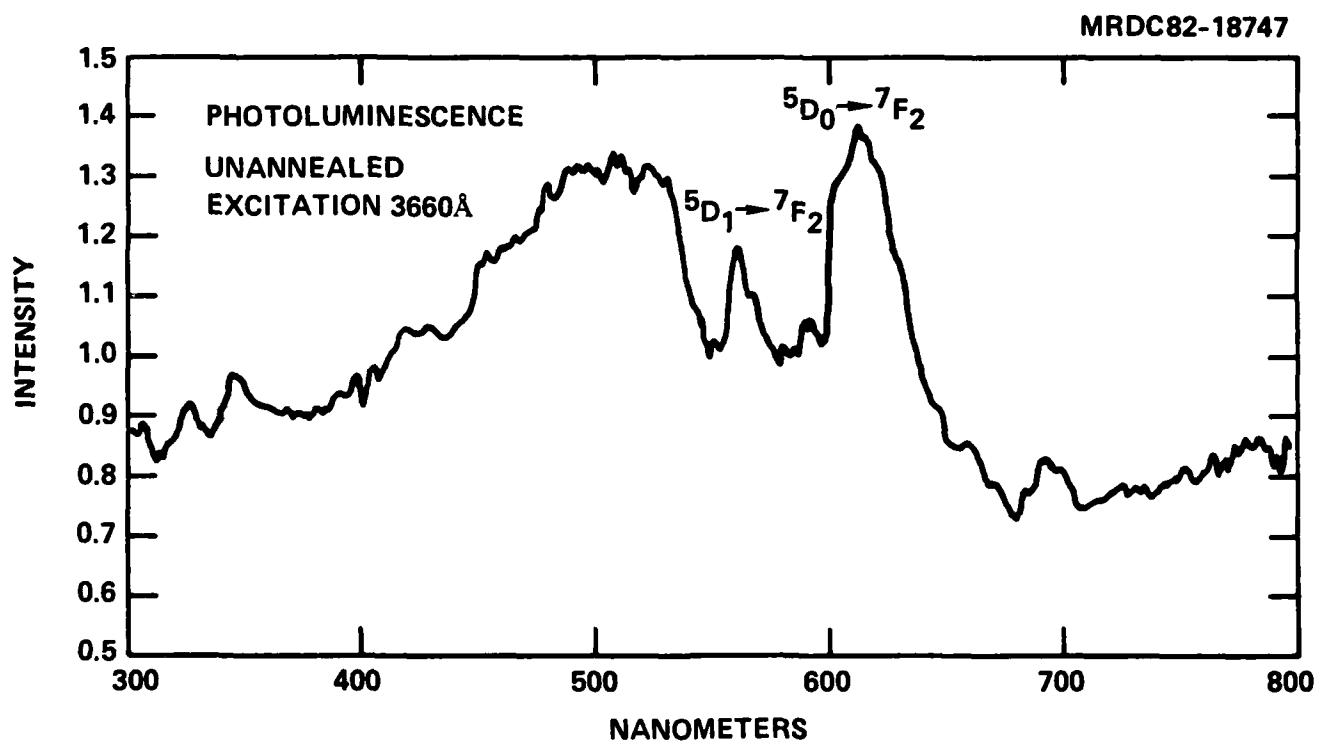


Fig. 8 (Cont.) (d) Unannealed film.



and that the shift in frequency is due to the disorder in the films.

As the anneal temperature is increased the intensity of the major peak at 6260 appears to go through a maximum at one hour. The absolute photoluminescence intensity at 6260 for the CRT powder is about 200 times as great as that of the Y_2O_2S films. Possible reasons for this are: 1) excess activator concentration so that the light is being concentration quenched; 2) internal light trapping due to the thin film nature of the emitter that only a small portion is emitted perpendicular to the film; and 3) greater phosphor volume of the powder sample compared with the thin film so that most of the exciting radiation is absorbed in the phosphor rather than in the substrate. It should be noted that in the case of an efficient zinc sulfide manganese activated film the ratio of 1000 to 1 exists when comparing an equivalent powder phosphor photoluminescence with the evaporated thin film form.

The photoluminescence spectra of the films which were annealed at 600°C for various times (1/2, 1, 5 hours) are shown in Figures 9a,b. The data shows that there is some improvement in the crystallinity as evidenced by the narrowing of the linewidth and increase in intensity. However, the improvement is about four times lower than the one hour anneal at 900°C. This important result seems to indicate that it will be difficult to



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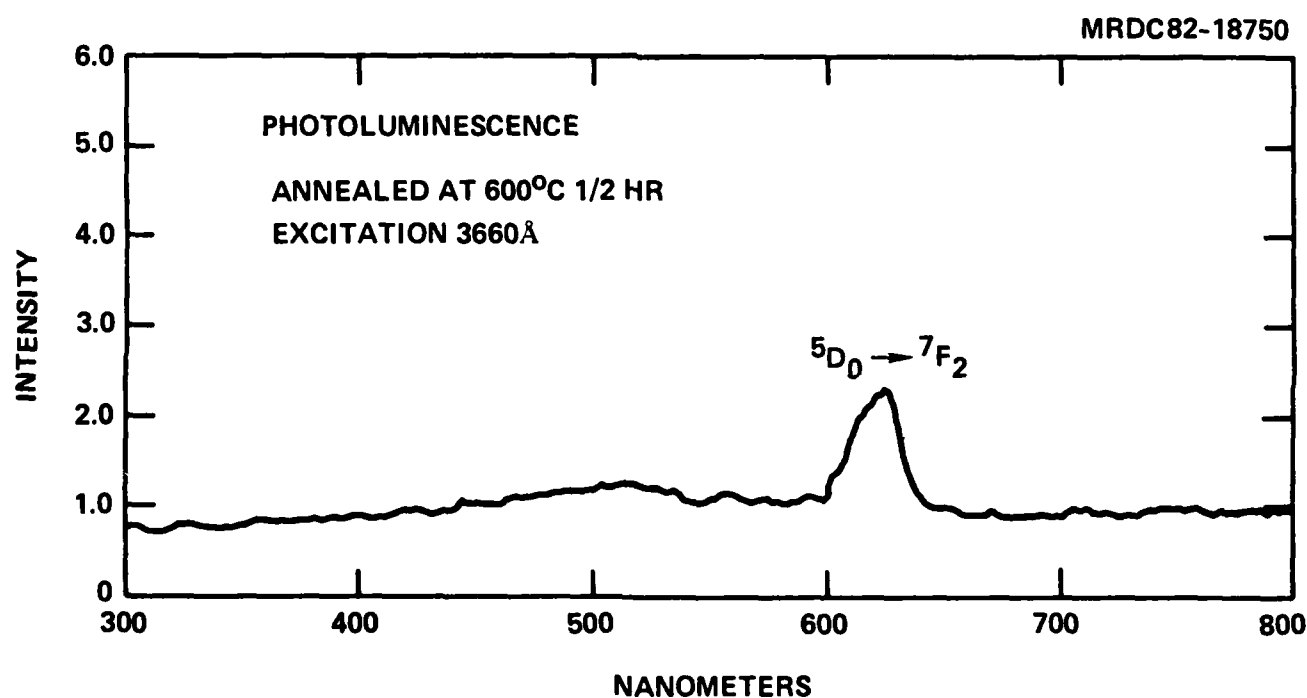


Fig. 9 Photoluminescent spectrum of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{+3}$ film on Al_2O_3 .
(a) Annealed for 1/2 hour at 600°C.

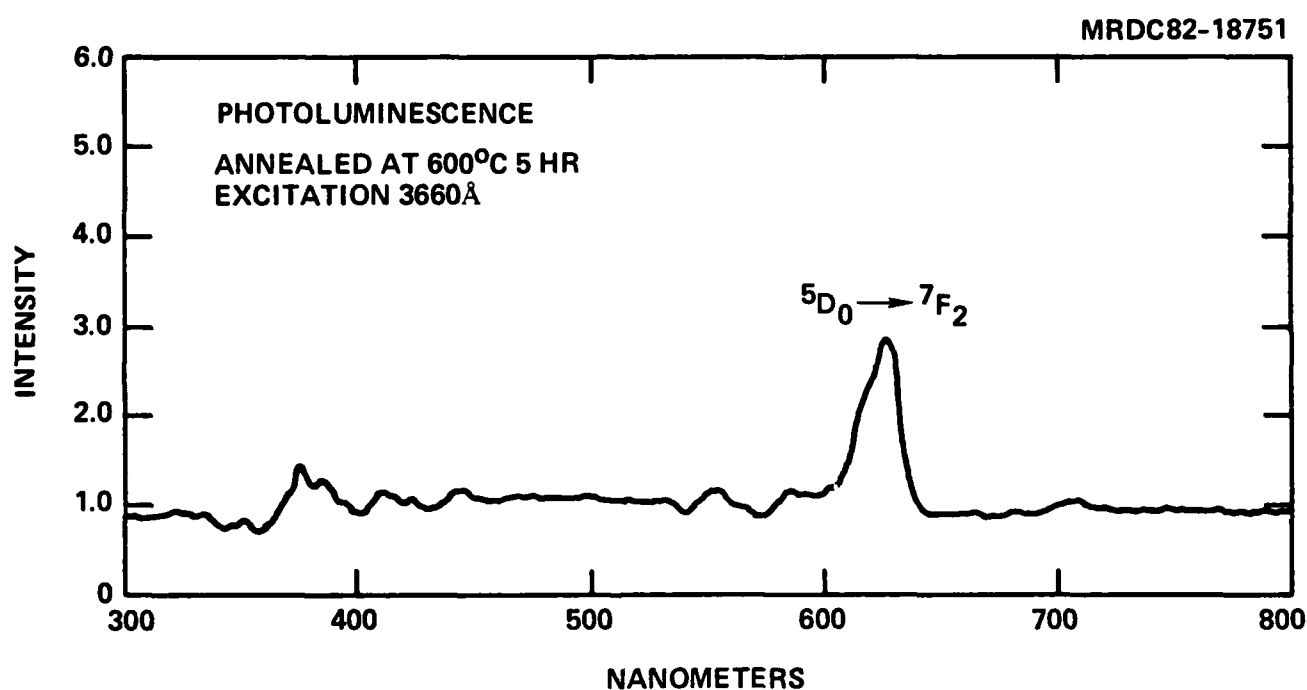


Fig. 9 (Cont.) (b) Annealed for 5 hours at 600°C.



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make the most efficient electroluminescent devices from the oxysulfide films on 7059 glass.

5.2 Electroluminescence Measurements

The room temperature electroluminescent emission spectrum of the $(Y_{1-x}, E_{ux})_2O_2S$ thin films is shown in Figure 10. A GaAs photomultiplier was used because of its flat spectral response in the visible region. The emission spectrum is characteristic of the Eu^{+3} ion.⁶ The dominant lines are due to the following transition, $^5D_1 \rightarrow ^7F_2$ (5656), $^5D_0 \rightarrow ^7F_1$ (5960), $^5D_0 \rightarrow ^7F_2$ (6720) and $^5D_0 \rightarrow ^7F_4$ (7070). These films were deposited on 7059 glass and were annealed for one hour at 600°C in argon.

The unannealed $Y_2O_2S:Eu$ devices showed no electroluminescence although they showed some photoluminescence. For electroluminescence to occur, the electrons in the host must be accelerated to energies sufficient to excite the activator. X-ray data indicates that the unannealed films are not very crystalline. It may be expected then, that the electron will give up much of its energy to the lattice through inelastic collisions.

Electroluminescent devices fabricated using ZnS as a host exhibit a steep nonlinear response of brightness as a function of voltage. The mechanism responsible for this nonlinear response can be explained as follows:⁵ charges from deep trap within the active layer are field ionized and swept to the interface between the dielectric and the ZnS layer where they are trapped. In the



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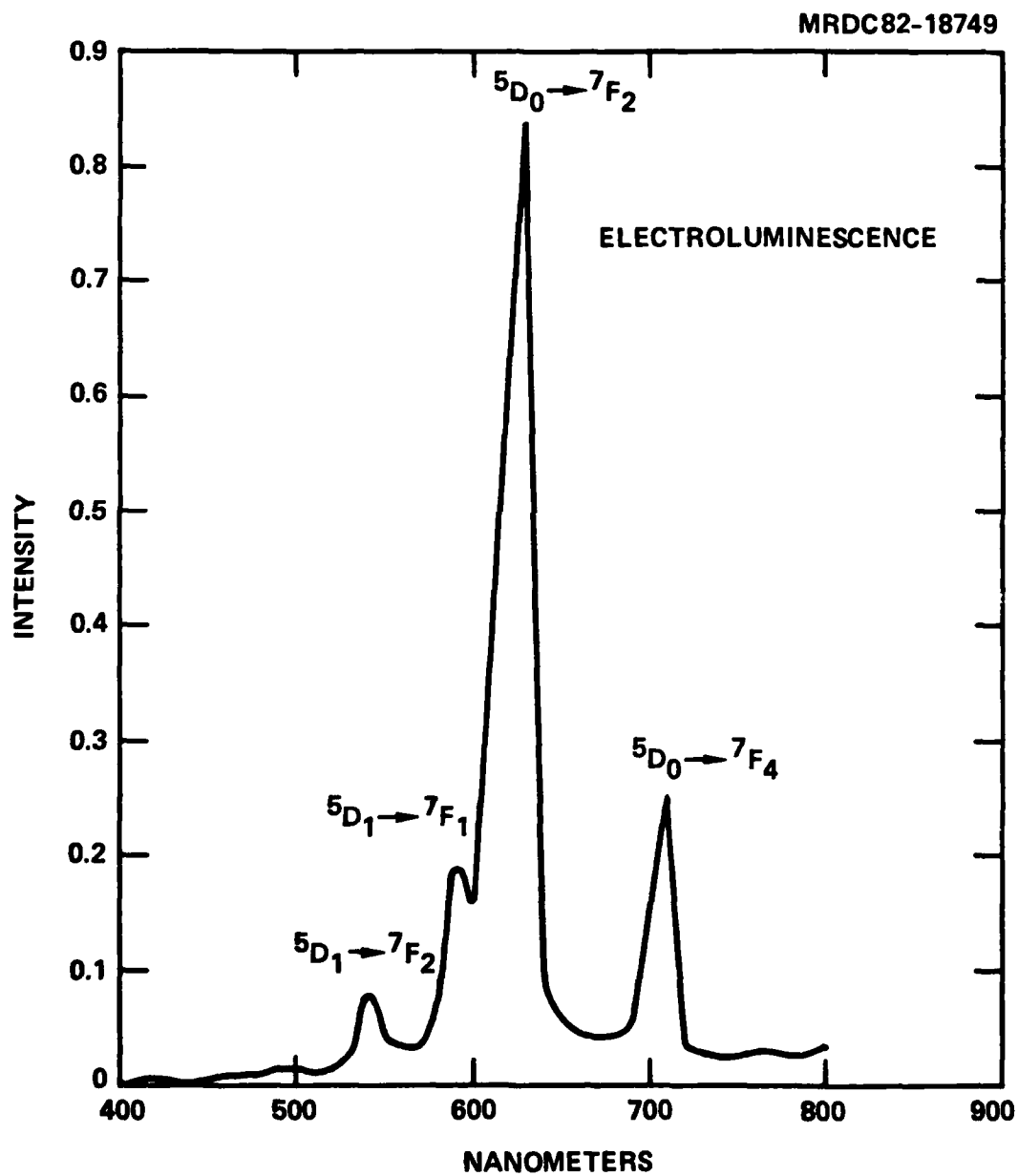


Fig. 10 Room temperature electroluminescent spectrum of yttrium oxysulfide film doped with Eu^{+3} .



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next voltage cycle they remain in their traps until the field reaches a sufficient level to allow the charges to tunnel through the barrier and become "hot electrons" very fast. These energetic electrons then impact excite the activator causing luminescence and are trapped at the opposite interface where they remain until the next half cycle of the voltage waveform. The process then repeats itself. It is this tunneling field emission which explains the steep nonlinear characteristics of these thin film emitters. Figure 11 shows the brightness-voltage characteristic of the Y_2O_2S films developed under this program. It can be seen from the plot that the slope is very shallow indicating poor charge injection from the interface. Previously the electronic current responsible for generating light was measured by placing a triangular voltage across the device and measuring the current. For a capacitor which exhibits no tunneling, the current waveform is a squarewave. However, for a device in which there is a tunneling current, this current is superimposed on top of the squarewave displacement current (see Figure 12). For a constant change in voltage the current is a constant until threshold is reached. Then the electronic current increases rapidly. With oxysulfide devices, the electronic component appears to continually increase during a greater portion of time that the voltage is increasing. This phenomenon could be the result of the energy levels of the interface states of these devices being much lower than comparable ZnS devices or that the oxysulfide devices are "lossy" i.e. have a higher



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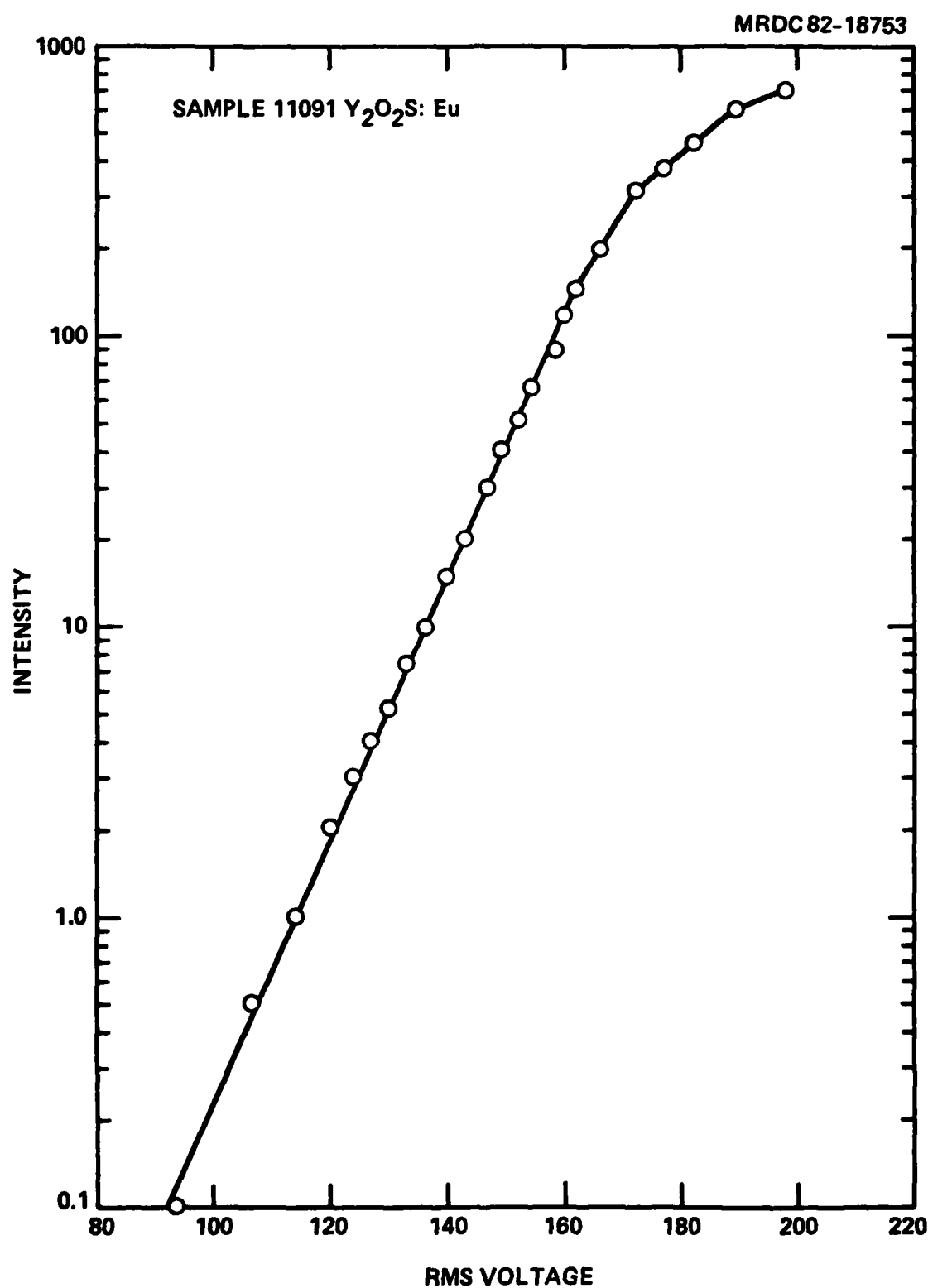


Fig. 11 Brightness-voltage curve for $\text{Y}_2\text{O}_2\text{S:Eu}^{+3}$ thin film emitter.



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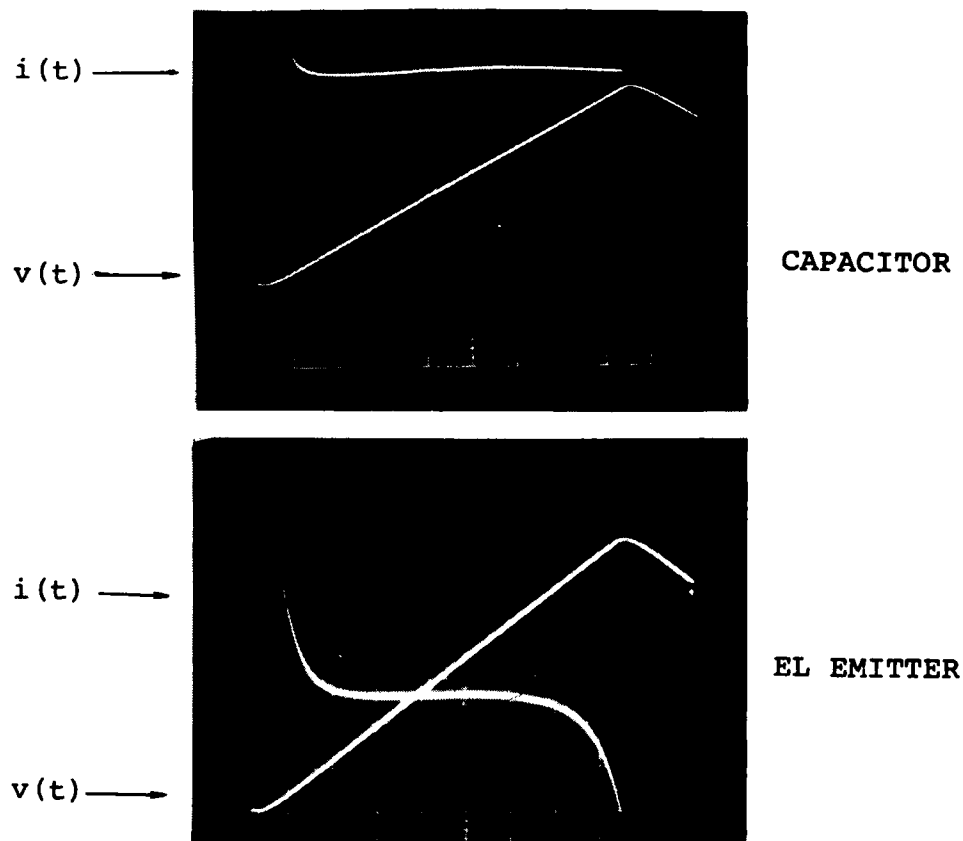


Fig. 12 Current and voltage waveform showing electronic component:
(a) capacitor; (b) EL emitter.



conductivity. This latter explanation appears to be the case for those devices that exhibit very low thresholds for electronic conduction. The total number of charges available for excitation is about 10^{11} , which is comparable to the ZnS devices. However, since the current starts at a much lower voltage, many of the electrons do not reach energies sufficient to impact excite the europium activator. Measurements of the current density of the annealed devices was extremely difficult because of cracks due to the anneal which caused electrical failures. Current measurements made on unannealed samples, which were not crazed, are shown in Figure 13. It is seen that these devices show a strong temperature dependence. A similar behavior is observed for unannealed ZnS films. However, the Y_2O_2S films started conducting at very low voltages for the higher temperatures. The interface trap depth as determined from the slope of the $\ln j_{\max}$ vs $1/F$ curves are about 0.2 ev as compared to 0.5 ev for the ZnS:Mn films. The conductivity observed with the unannealed Y_2O_2S films appears to have an inverse temperature dependence. This type of behavior can be explained by either Schottky or Poole-Frenkel mechanisms. At present insufficient information is available to select one mechanism. The important observation is that the mechanism for unannealed ZnS films is different than for annealed ZnS films and that similar results may be true for Y_2O_2S films.



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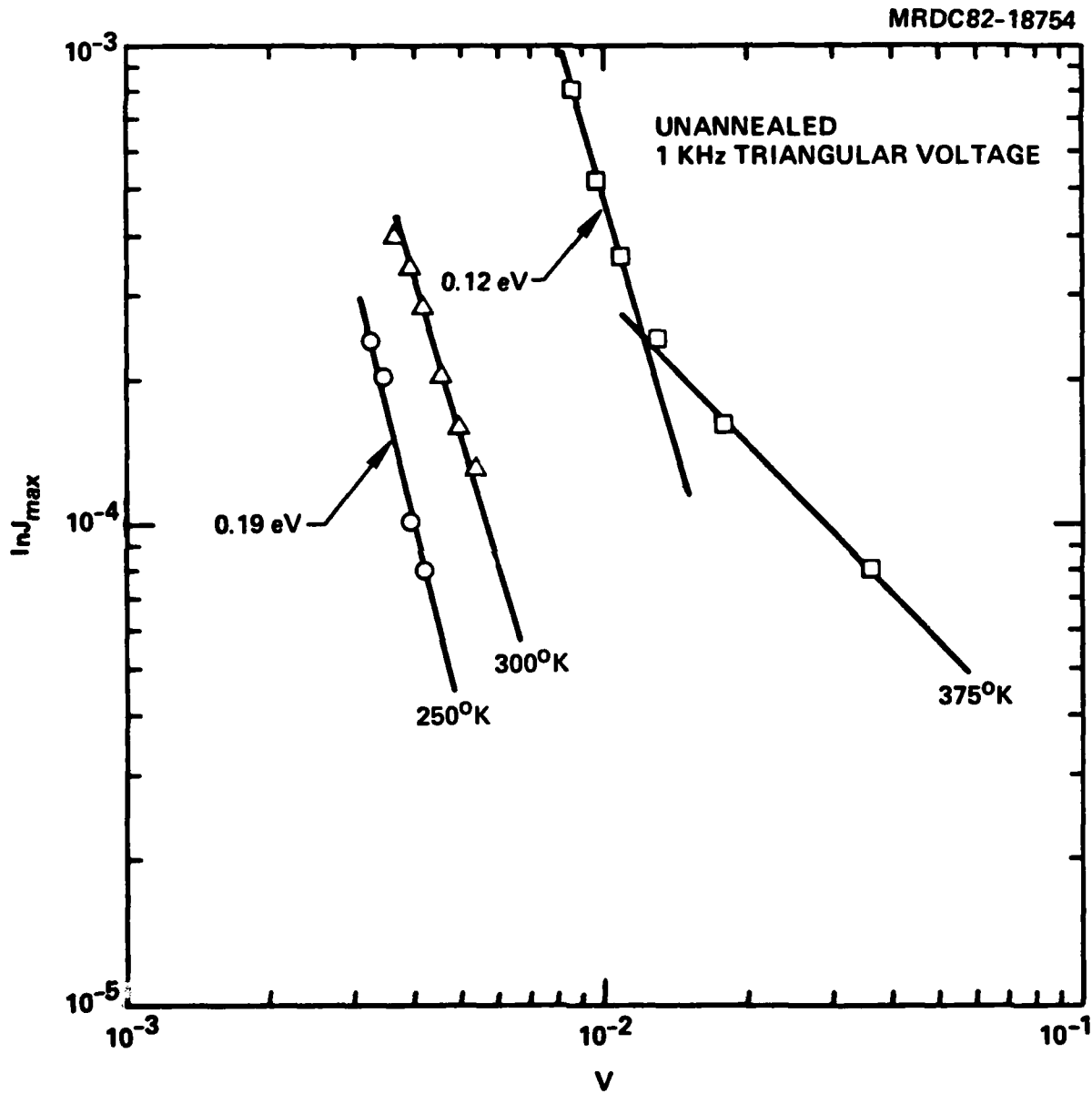


Fig. 13 $\ln J_{\max}$ vs $1/F$ for unannealed $Y_2O_2S:Eu$ films at 250°K, 300°K and 375°K.



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In general, the tunnel injected current associated with EL emission in ZnS:Mn devices has only been observed on unannealed oxysulfide devices. The unannealed samples exhibited either no tunnel current or very small currents which appear at fields where the films experience dielectric breakdown. One explanation is that the traps at the interface, where the charges are assumed to reside, are much deeper in the annealed oxysulfide films than in comparable ZnS devices, thereby requiring a higher field before they can tunnel out.

In an effort to increase the in-phase current available, a layer of ZnS was added next to the $Y_2O_2S:Eu$ layer. It was assumed that charges created in the ZnS layer would be injected into the oxysulfide to enhance the probability of excitation of the Eu activator. The result of this experiment indicated that there was a significant in-phase current. However, no electroluminescence from the Eu^{+3} activator was observed. There was some broadband emission which appeared light blue in color. This emission is very similar to the emission observed with ZnS without an activator and is assumed to be due to self activation. Another possible problem with this run was the europium concentration was very low. Also, it is possible the majority of the field appeared across the ZnS layer and the resulting field across the oxysulfide was not sufficient to accelerate the charges to high enough energy to impact excite the europium ions.

The energy of the 5D_3 level of the europium ion appears to coincide with the conduction band of the oxysulfide host.⁷



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Therefore, it is possible for energy transfer to exist between the electronic levels of the host and the electronic levels of the activator with a subsequent relaxation process within the band system of the host. Presumably, this would occur with the EL devices since these films show poor crystallinity as observed with both x-ray diffraction data and photoluminescence.

In evaluating the data on an electroluminescent emitting device compared to other oxysulfide devices it appears necessary to incorporate a metal ion such as copper or zinc in small quantities. These may act as sensitizers in which excited electrons and holes created at sensitizers are transferred to the conduction and valence bands and are available for impact excitation of the activator ion.

5.3 Transmission Measurements

Absorbtion measurements were made on the oxysulfide films deposited on sapphire. Figure 14 shows the transmission spectrum of a typical annealed film in the visible region. From this data it was determined that the band gap of the material is 4.5 eV. Similar measurements made on the yttria indicate that its band gap is 5.8 eV. Measurements on ZnS films indicate the band gap to be 3.5 eV.

5.4 Dielectric Constant

In order to determine the dielectric constant of the oxysulfide films, capacitors were fabricated by depositing the



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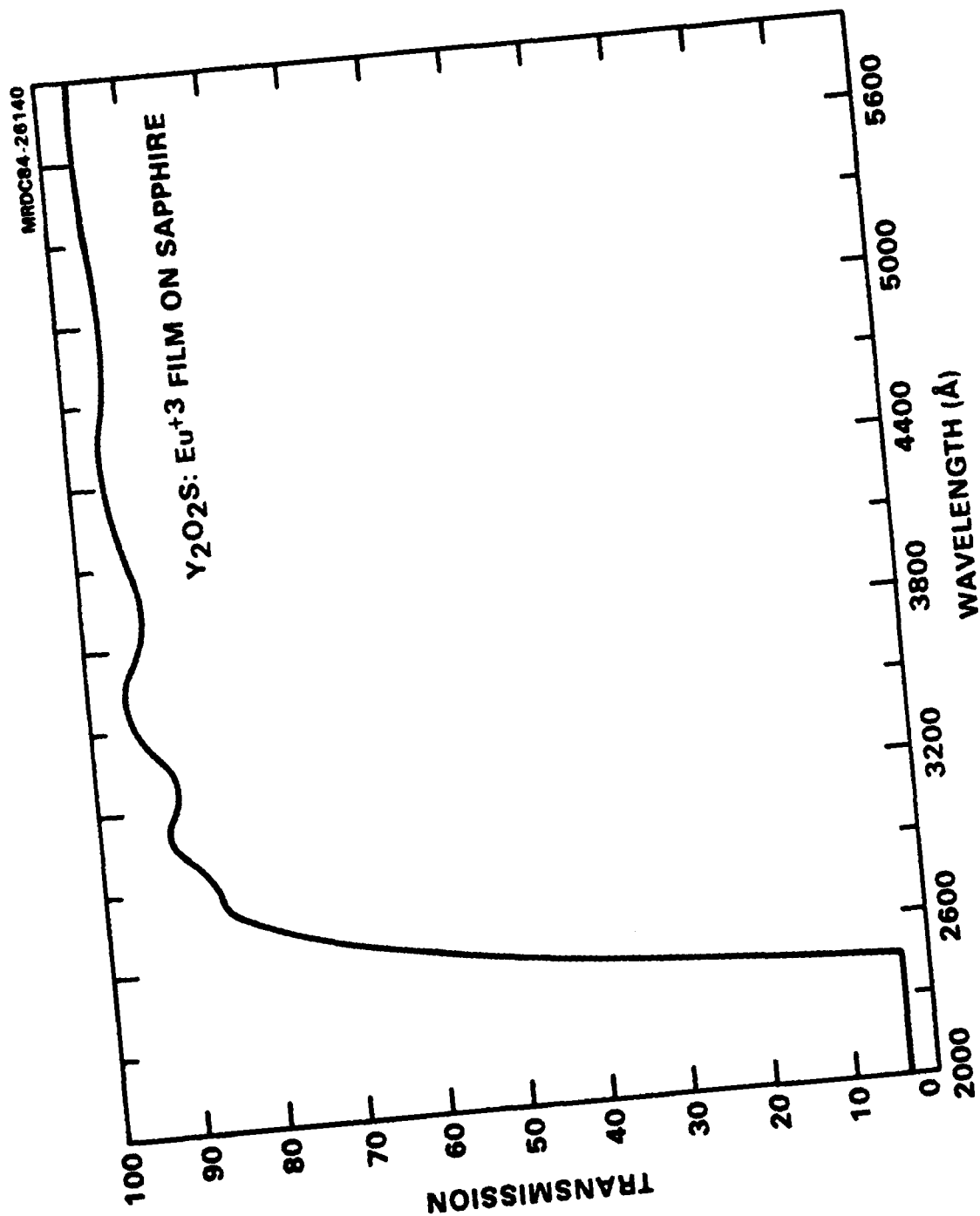


Fig. 14 Transmission spectrum of $\text{Y}_2\text{O}_3\text{S:Eu}^{+3}$ thin film.



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film on ITO coated glass, with overlaying top aluminum electrodes. The thickness of the film was determined with a Dektak profilometer. The dielectric constant was determined to be eight with a dissipation of 0.009.



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6.0 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The objective of this program was to investigate the feasibility of fabricating $Y_2O_2S:Eu$ thin film ac electroluminescent devices. For the first time, electroluminescence was observed in thin films of rare earth host phosphors. As a result of this work it has been determined that efficient cathodoluminescent thin films can be fabricated using E-beam deposition techniques similar to that required for high quality dielectric films used in conventional electroluminescent emitters. These films exhibited a desirable narrow band emission associated with the europium activator. However, the EL intensity was low (fractions of a ft-L) due to the physical limitations of the film so that a high electric field could not be applied to the final device. Prerequisite for cathodoluminescence in these films was an annealing step at elevated temperature. Films consistently crazed after this annealing step when fabricated on 7059 glass. The crazing in turn induced cracks in the film so that a high electric field could not be applied across the film.

The micro-cracks are influenced by: a) the rate of heating and cooling during the anneal cycle; b) reaction between Y_2O_2S and ITO films at the elevated temperatures necessary for anneal; c) the stoichiometry of the Y_2O_2S film prior to anneal; d) the coefficient of expansion difference between the substrate and oxysulfide film.



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Electroluminescence was observed only in films that also exhibited cathodoluminescence. Therefore, it may be concluded that cathodoluminescence is a necessary but not sufficient condition for electroluminescence. In order to obtain electroluminescence in the oxysulfide films it may be necessary to incorporate an appropriate metal ion.

Annealing studies at various times and temperatures conducted with an aluminum oxide (Al_2O_3) substrate material indicated that a 4-fold improvement in brightness could be obtained in the photoluminescence if temperature of 900°C were used instead of the 600°C as limited by the glass substrate typical of the conventional thin film EL emitter.

Future work will focus on lowering the anneal temperature requirements. In addition, further work is necessary to reduce the microcrazing that occurs during the anneal cycle. Further investigation will be necessary to determine the role that metal ions play in enhancing electroluminescence.



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